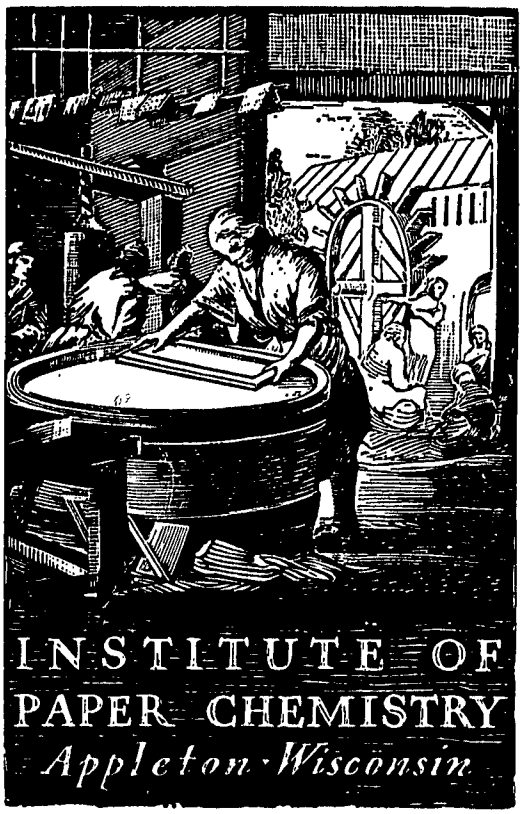

COLOR REMOVAL FROM KRAFT MILL EFFLUENTS BY ADSORPTION AND ULTRAFILTRATION

Project 3254

Report One
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

May 28, 1977

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

The degree of color removal from pulp and paper mill effluents required by proposed government regulation has necessitated the evaluation of a variety of methods for color removal. Kraft mills which bleach pulp have significant color removal problems with the chlorination and the caustic extract stage effluents. Although decolorization of these effluents by physicochemical methods such as resin adsorption and ultrafiltration is feasible, highly concentrated, low volume streams are produced which need to be handled. Prior to rigorous economic evaluation of these processes, more laboratory and pilot plant data are necessary.

Analysis of the data indicates that the chlorination stage effluent should be mixed with the caustic stage effluent to control pH and to allow the adsorption process to function at a lower overall color removal level while still meeting discharge guidelines. Costs seem competitive with the massive lime process. The data also show that the process is not very sensitive to raw material mix, although there are some differences between removal of color from bleached softwood and hardwood effluents. The resin was shown to be highly effective at elevated temperatures, but no long term, high temperature studies were conducted.

This work confirmed work done by a resin supplier that costs for color removal by adsorption would be about $1.50/ton. Resin suppliers are continuing to conduct studies of color adsorption and thus there is no need for the Institute to continue efforts in this area at this time.

Ultrafiltration was also tested for color removal. A polysulfone membrane was shown to have excellent color and solids rejection at high pH and temperature. Long term studies indicated that there was a general decline in flux rate, but no apparent damage to the membrane. Flux rates could probably be restored by cleaning.

Unlike the adsorption studies in which the concentrated color solutions could be added to the white liquor system and, thence, to the recovery furnace, the ultrafiltration concentrate must be further treated before discharge to the environment. Any economic studies must then cover the ultrafiltration process and the ultimate disposal process. No economic data were generated in the ultrafiltration portion of the project as the membranes were of an experimental nature. However, the preliminary results indicate that ultrafiltration could be a viable means of preconcentrating bleach effluents.

Color concentration by membrane techniques is viable. We are continuing to pursue this area in order to obtain data which will allow a fuller assessment of economic feasibility.

Although economic comparisons of the two processes are not possible, several technical comparisons can be made. In the adsorption process it is economically desirable to mix portions of the chlorination stage effluent with the caustic stage effluent to control pH. This results in roughly doubling the volume to be treated. Ultrafiltration, on the other hand, can treat the highly colored caustic effluent directly with high color removal. Significantly smaller volumes are thus treated. Color removal by adsorption is highly pH dependent and, therefore, the process is very susceptible to plant upsets. Ultrafiltration is not pH sensitive, so long as the membrane is not attacked and, therefore, is more likely to function at a high removal level in spite of process upsets.

PART I. COLOR REMOVAL BY ADSORPTION

INTRODUCTION

Decolorization of mill effluents by adsorption and ion exchange have been reported by several investigators (1,2). Pilot-plant and laboratory experiments have been used to estimate process economics. Very little data have been accumulated which would test these resins on a variety of pulp mill waste streams and over a wide variety of mill operating conditions. The goal of the first part of this work was to test a resin with different effluents and obtain sufficient data for preliminary economic analysis.

Three resins which have been proposed for use with bleach effluents were screened for suitability for long-term tests. These resins were Dow Chemical's XD 8704.03, Rohm & Haas' XE-275, and Rohm & Haas' Amberlite XAD-8. A number of experimental problems, including high back pressure with some effluents and deactivation of the column due to chlorine caused the XD 8704.03 and XE-275 resins to be rejected for further work. Therefore, all further process studies were conducted with the Rohm & Haas XAD-8 resin.

EXPERIMENTAL

Three hundred grams of Rohm & Haas Company Amberlite XAD-8 resin were placed in a 2.5-cm diameter column, giving a bed 61-cm high and a bed volume (BV) of 300 cc. Downflow feed rates varied from 2-12 BV per hour. The feed was prefiltered through Whatman No. 10 filter paper or a fiberglass pad prior to pH adjustment with H_2SO_4. Resin regeneration consisted of desorbing the adsorbed color with 1N, 0.5N, or 0.25N NaOH followed by a water wash and then acidification with 0.25N H_2SO_4

Color was measured by the NCASI method using Pt-Co as the reference standard (3). Adsorbance at 280 nm was measured with a Beckman DK-2A spectrophotometer in 1 cm cells after suitable dilution. Suspended solids were determined by the APHA standard procedure using a 5-micron Millipore filter.

Elevated temperatures were obtained by wrapping a heating tape around the column. The heating tape extended above the resin bed to form a feed preheater section. Temperature was recorded only for the column effluent, and it was assumed that this effluent temperature represented the column temperature.

Bleach plant effluent was applied to the column at an approximately constant rate with a positive displacement pump from a reservoir tank. The column effluent was collected in 5 to 10 equivolume samples. Portions of these samples were then analyzed for color. TOC and suspended solids were run on selected samples.

Feed materials for this study were obtained from a bleached kraft mill where about 380 tons per day of pulp are bleached by a CEDED sequence. Table I summarizes the important characteristics of these effluents.

The samples were obtained over a period of about 6 months and it is interesting to note the shift from higher softwood use to higher hardwood use by the mill. This shift points out the requirement that any treatment process be able to accommodate an extremely variable input.

RESULTS AND DISCUSSION

Initial adsorption of color varied between 80 and 95% depending on temperature. As effluent was continuously applied to the column the total color adsorption decreased as expected. Table II and Fig. 1-5 summarize the results.

TABLE I

ANALYSES OF ALKALINE EXTRACTION STAGE EFFLUENT SAMPLES

Feed No.	Wood Type,[a] %	24-Hour Solids, g/l	OD[b]	Color, mg/l	Suspended Solids, mg/l	BOD_5, mg/l	pH	COD,[c] mg/l	TOC,[d] mg/l
121	75 SW	3.82	23.0	8217	184	226	11.4	2850	1030
123	75 SW	2.26	12.5	5240	48	67	9.7	1380	500
127	75 SW	3.53	21.9	9200	23	288	11.3	1814	720
131	80 HW	2.58	11.2	3480	22	228	11.4	1158	450
122[e]	--	1.01	2.9	296	--	--	8.4	--	--
124[f]	75 SW	1.21	2.2	700	--	--	2.1	--	--

[a] SW = softwood
HW - hardwood.

[b] OD = optical density at 280 nm.

[c] COD = chemical oxygen demand.

[d] TOC = total organic carbon.

[e] Total mill effluent.

[f] Chlorination stage effluent.

Table II indicates that when 15 to 20 bed volumes (1 liter = 3.3 bed volumes) of kraft bleach effluent had been applied to the bed, cumulative color removal had dropped to 50 to 60%. Based on other data, instantaneous color adsorption (the ratio of effluent color to feed color) dropped to 40 to 50%. This change has implications for column design. If the effluent from the unit is discharged to a further treatment facility with a long hold-up time and is well mixed, the cumulative removal of color will be the design guide. On the other hand, if succeeding treatments are rather quick, it will be necessary to always have the color removal at a high level and the important design criteria will be the instantaneous

TABLE II

ADSORPTION OF COLOR FROM ALKALINE BLEACH EFFLUENTS ON XAD-8 RESIN

		Loading							Regeneration			
Run No.	Wood Type	Feed No.	pH as Received	pH Adjusted	Temp., °C	Feed[a] Volume, liter	Flow, BV/hr	Color Removed, %	NaOH, N	NaOH Volume, liter	Flow, BV/hr	Color Recovery, %
1	75% SW		10.3	NA								
2		123	10.3	2.0	24	6	2	68	1	0.75		91
3		123	10.3	2.0	24	6	12	54	1	0.75	2	90
4		123	10.3	2.0	24	3.5	12	69	1	NA	2	
5		123	9.18		24		6		1	1.50	2	
6		123	9.18	1.8-2.0	24	6.6	12	69	1	0.75	2	
7		123	9.7	2.0	24	5	12	57	1	0.75	4	
8		123	9.7	2.0	24	5	12	55	1	0.75	4	
9		123	9.7	2.0	24	5	12	56	1	0.75	4	
New Resin												
14		127	11.3	2.0-2.5	24	5	12	58			3	128
14A		127	11.3	2.0-2.5	24	5	12	47	0.25	2.5	3	98
15		127	11.3	2.0-2.5	24	5	12	42	0.25	2.5	3	88
18		127	11.3	1.9	33	3.5	6	63	0.5	1.5	3	100
19		127	11.3	2.5	39	3.5	6	65.2	0.5	1.5	3	94
20		127	11.3	2.5	25	3.5	6	51.2	0.5	1.5	3	96
21		127	11.3	2.5	60	3.5	6	86.4	0.5	1.5	3	85
22	80% HW	131	11.4	2.5	60	3.5	6	77	0.5	1.5	3	NA
23		131	11.4	2.3	60	12.6	12	62.3	0.5	1.5	3	89
24		131	11.4	2.3	18	4	12	40	0.5	1.5	3	115
25		131	11.4	6.3	60	1.8	12	20.4	0.5	1.5	3	94.3
26		131	11.4	3.9	60	3.9	12	57.3	0.5	1.5	3	95.5

[a]Conversion factor, 3.3 BV/liter.

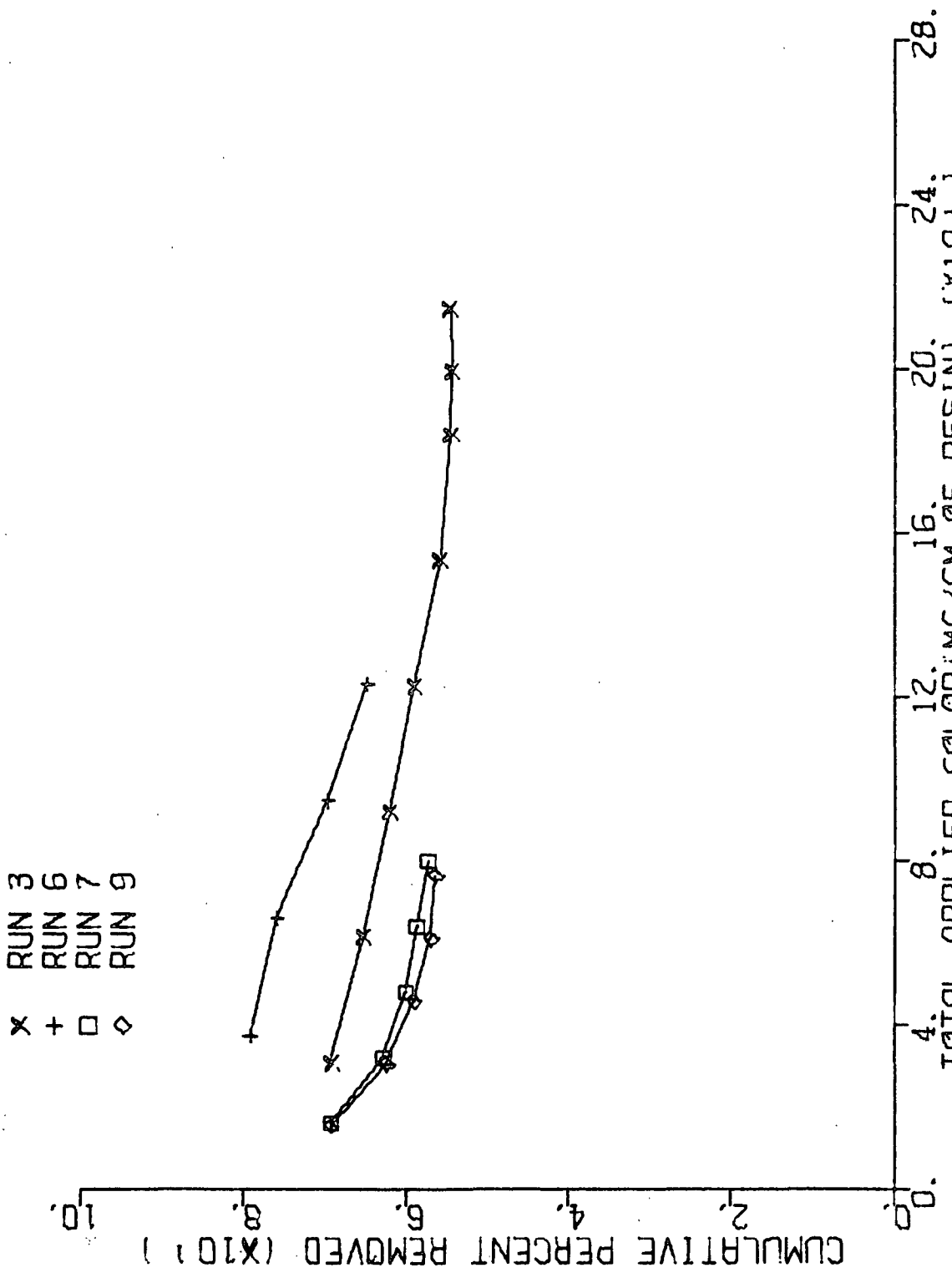

Figure 1. Color Removal from Softwood Bleach Effluents

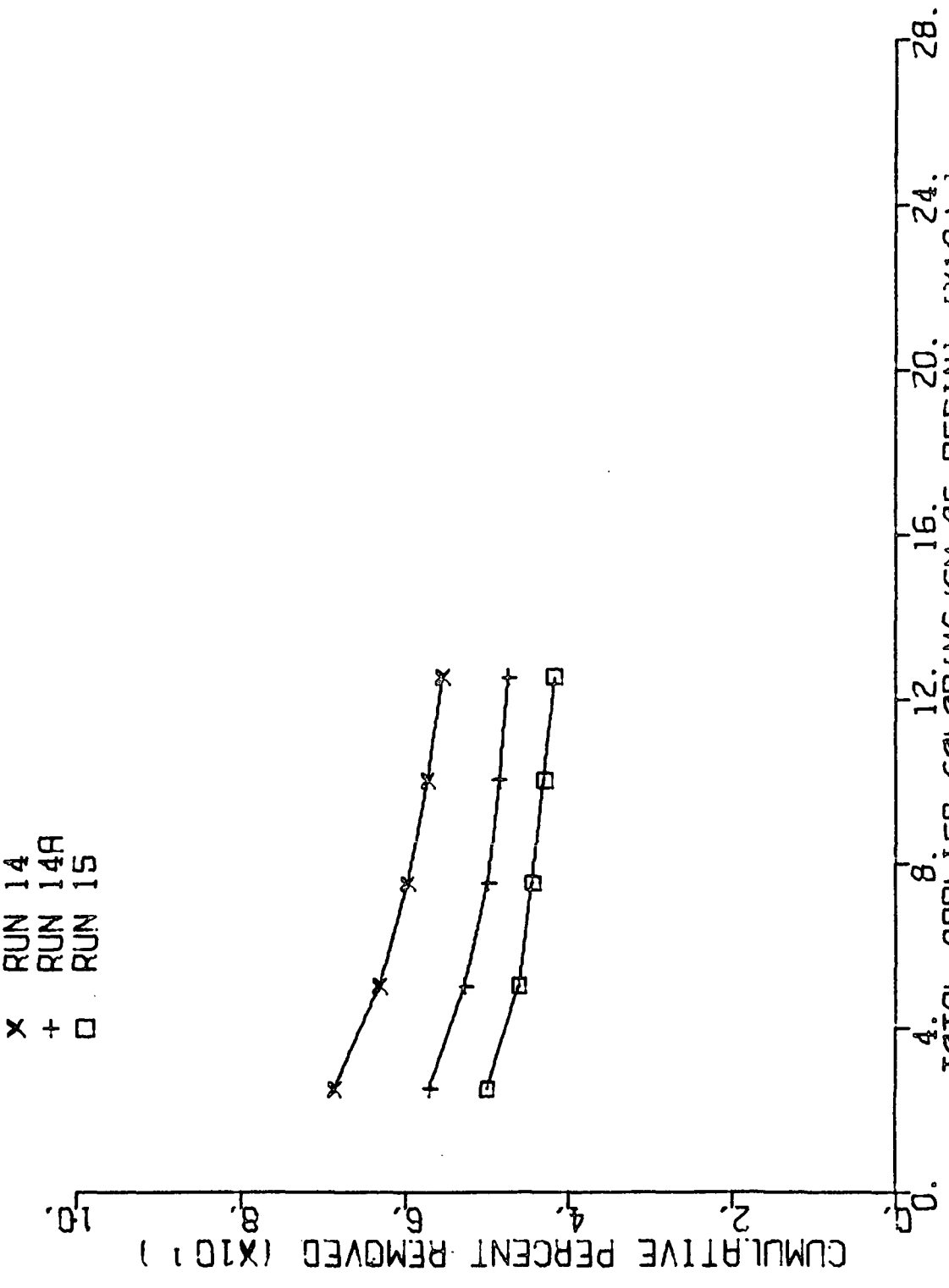

Figure 2. Decreasing Color Removal with Increasing Regeneration Cycles

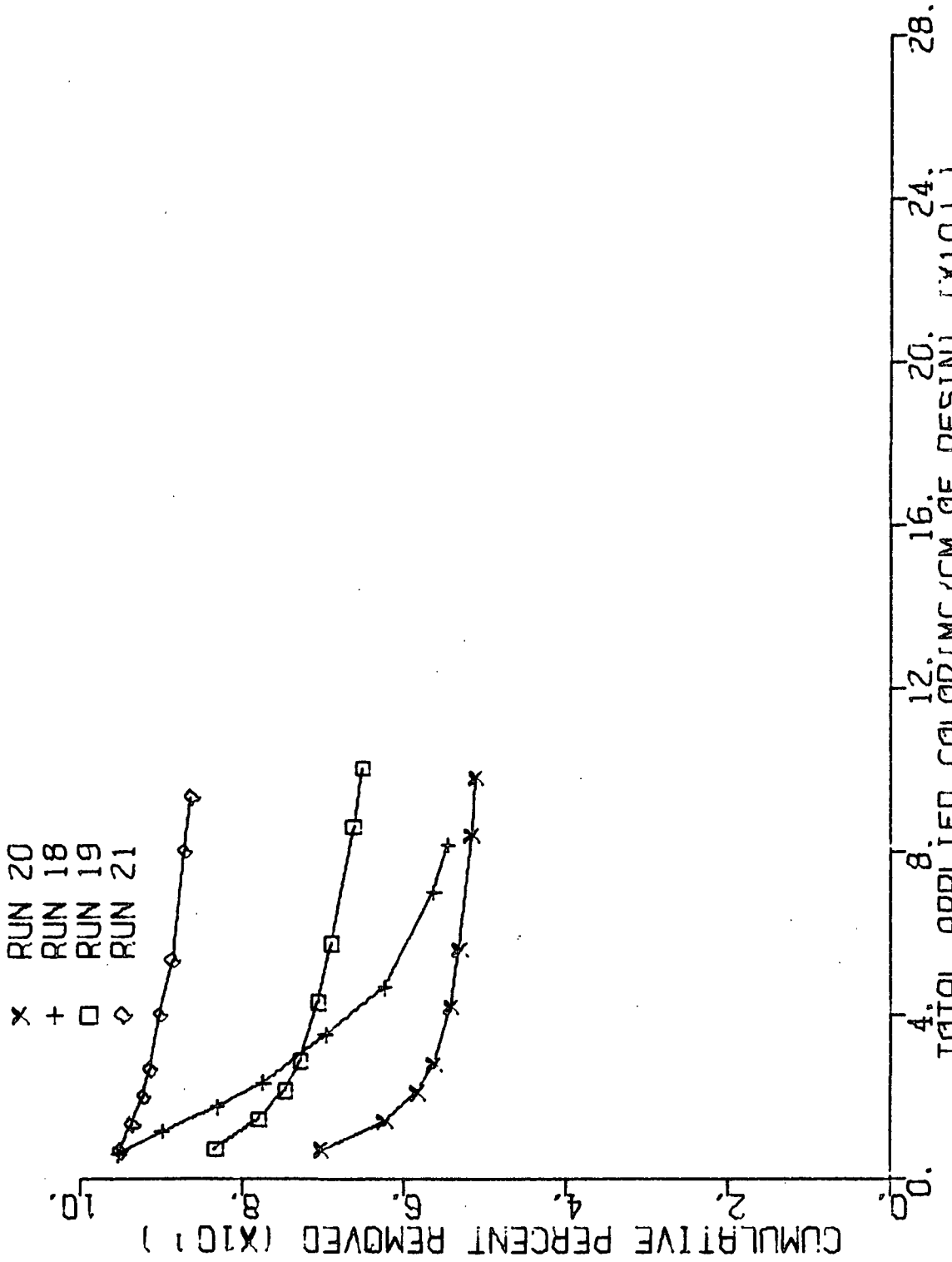

Figure 3. Effect of Temperature on Color Removal from Softwood Bleach Effluents

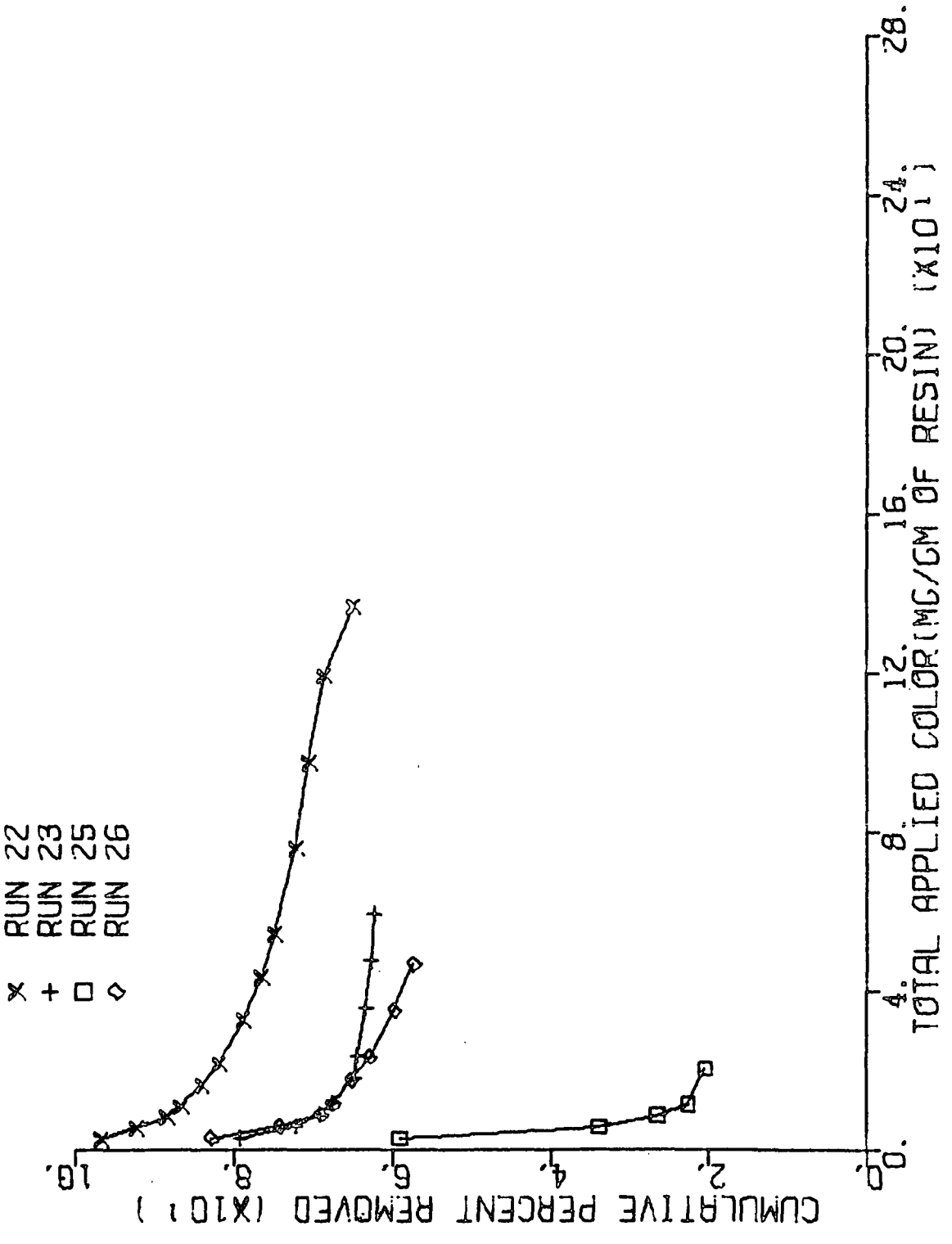

Figure 4. Color Removal from Hardwood Bleach Effluents

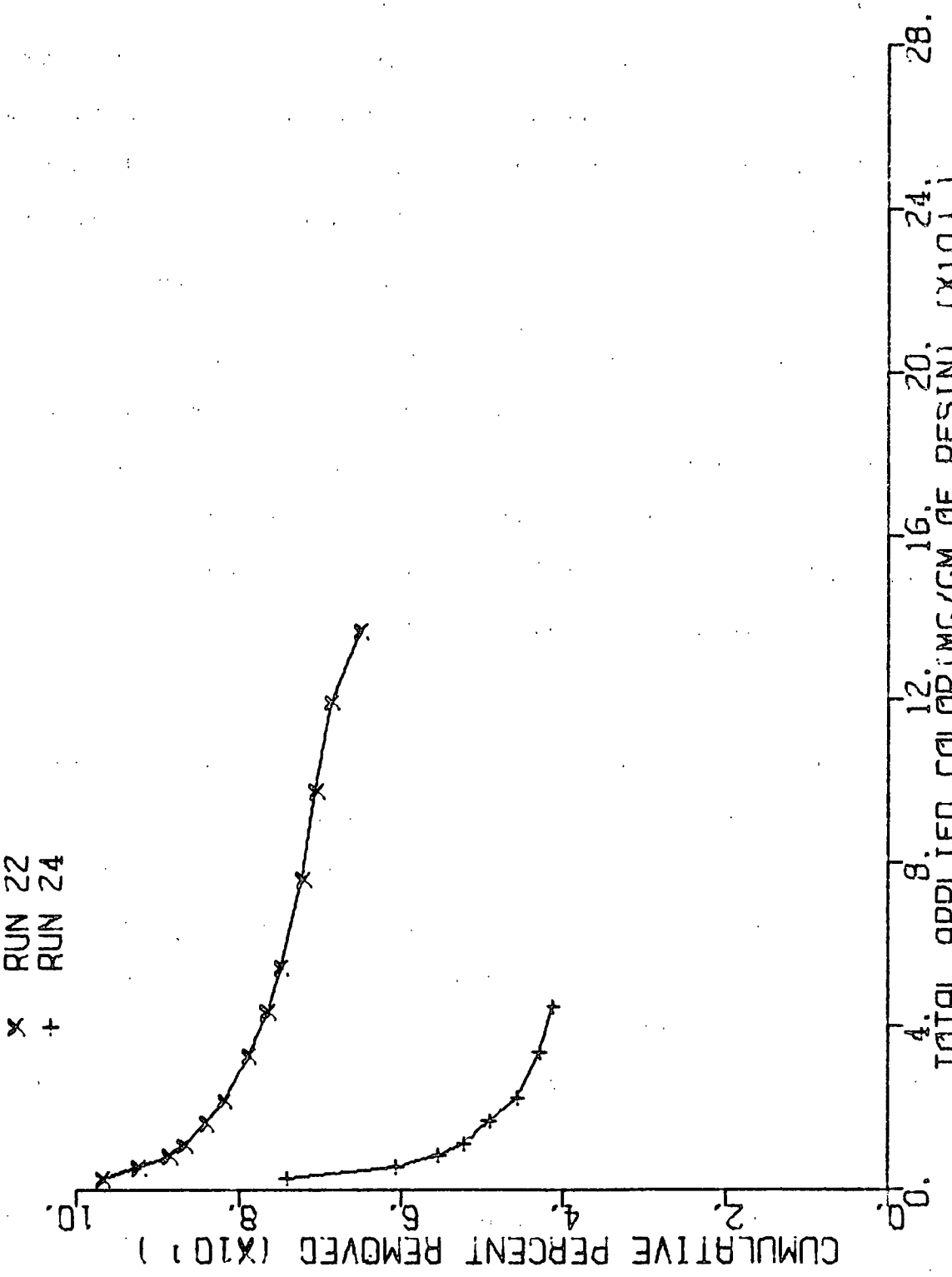

Figure 5. Effect of Temperature on Removal of Color from Hard Bleach Effluent

color removal rate. However, for purposes of discussion, it will be assumed that cumulative color removal is the important design factor. Use of the cumulative color removal as a performance criterion is in line with proposed regulations setting a limit on the total amount of color that can be discharged. Should regulations be changed to control instantaneous color levels on the effluent, then the instantaneous color removal might be the important design guide.

Figure 1 indicates that color removal is not a function of feed rate in the range of 2 to 12 bed volumes per hour. Cumulative color removal appears to depend primarily on the total color applied to the column. This would indicate that the adsorption equilibrium between the solution and sorbed phase is established relatively quickly. If the sorption process were slow relative to the feed rates used in this experiment, there should be a difference between color removal at the two extreme feed rates.

Individual curves in Fig. 1 indicate that decreasing amounts of color are adsorbed on each cycle. A new column was prepared and three successive runs were made under identical conditions. As shown in Fig. 2, the amount of color adsorbed decreased between each cycle. Since virtually all of the color was recovered, as indicated in Table II, something must be destroying adsorption sites in the resin. The degree to which this resin degradation continues with increasing adsorption/regeneration cycles must be studied before accurate economic data can be formulated.

Temperature also affects the operation of the resin column. Figure 3 indicates that rather large increases in adsorption can be obtained with increases in temperature. The reason behind this increase could be many fold, including a

change in the adsorption equilibrium constant, increased number of available adsorption sites, and swelling of the resin to expose more surface. Increased flux rate due to higher diffusion coefficients with the pores of the resin could also be a contributing factor. The high adsorption at high temperatures is important from an economic standpoint as it means that the alkaline bleach effluents can be treated without need for cooling. Neutralization will also help maintain the higher temperatures. The effect of temperature on the life of the resin was not investigated. Color recovery, as shown in Table II, Runs 18-21, is quite high for all temperatures (25-60°C).

Color removal by adsorption must be capable of handling a variety of feed stocks. The previous experimental results were for a bleach effluent from a mill pulping about 75% softwood. Figure 4 shows adsorption results when the mill was pulping a mixture containing about 80% hardwoods. Color removal as indicated by Table II, Runs 23 to 26, and Fig. 4 was a bit lower than for softwoods but still quite high.

The operating temperature also had a noticeable effect on color adsorption from the hardwood bleach effluent, as shown in Fig. 5. From the limited data, it appears that the adsorption of color bodies from a hardwood bleach effluent is affected to about the same degree by temperature as the effluent from bleaching a softwood pulp. As with a softwood bleach effluent, operation at the higher temperature is desirable because it eliminates the need for cooling the effluent and it increases the adsorption.

The effect of pH was also studied on the bleach effluent from the hardwood pulp. As shown in Fig. 4, adsorption is drastically reduced as pH is increased. The optimal pH must be obtained by balancing reagent costs vs. adsorption column size and regeneration schedules.

Color removal from pulp wash waters and a soda recovery effluent were attempted. However, precipitates formed when the pH was lowered and the decolorization runs could not be made.

PROCESS OPERATION

Before considering the economics, a brief description of the operation of an adsorption decolorization unit is necessary.

A simplified schematic is shown in Fig. 6. During a loading cycle, bleach effluent is fed from the storage tank to one of the columns (call it Unit A). This continues until the unit is totally loaded (normally determined as a fixed amount of time based on experimental data). The bleach liquor is then diverted to another column (call it Unit B). White liquor (or weak wash) is then fed to Unit A to start the regenerating process. When this feed is started, the column is filled with highly colored bleach liquor which must be displaced and recycled to the bleach liquor storage tank. Approximately 0.4 of a bed volume should be recycled in this manner. The regenerating solution effluent is then diverted to the white liquor system. The regenerating solution is applied to the column for a fixed period of time. At the end of this period, the column is loaded with the regenerating solution and it is ready to receive more bleach liquor. As bleach liquor is applied to the column, the regenerating solution is displaced and fed to the white liquor system. To ensure total recovery of the sodium, a volume in excess of one bed volume should be sent to the white liquor system. After the regenerating solution is displaced, the column must be reacidified. The combined chlorination stage and caustic stage effluent (pH $\approx$ 2.5) can be used. However, no decolorization takes place and this liquor must be recycled.

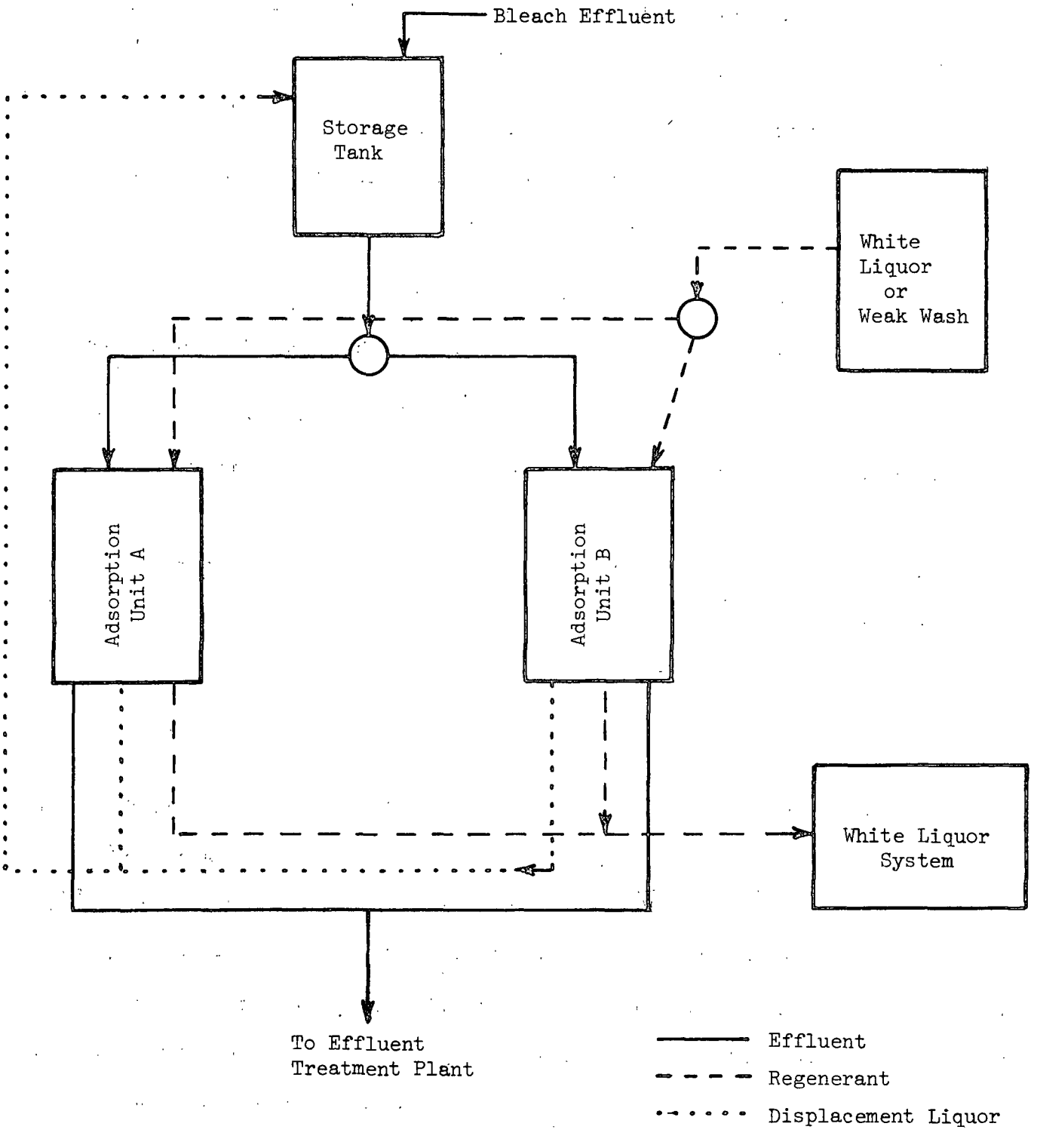

Figure 6. Simplified Adsorption Flowsheet

Rock, et al. (1) in their pilot-plant studies estimated these displacement volumes to be (with white liquor as a regenerant):

Displacement volumes to be recycled for color removal:

0.4 BV from displacement of bleach liquor by regenerant

5.7 BV from reacidification step

Excess volume to white liquor system:

0.4 BV from displacement of regenerant from reacidification step.

The bleach liquor used to reacidify the bed changes very little in color. Thus, its effect on the color balance can be ignored. The important factors to consider are the time required for the reacidification step and the cost of equipment to store and pump this liquor. This time must be included as part of the regeneration step.

PROCESS ECONOMICS

Pretreatment

Raw bleach effluent contains suspended solids which collect on the resin bed. It has been suggested that sand filtration could control the accumulation of these solids (1). If a sand filter is used with particles of diameter similar to that of the resin bed, then suspended solids passing through the sand filter will also pass through the resin bed. Provision should be made for backwashing the resin bed in case of suspended solids entrapment, however. Cost for prefiltration should be similar to that encountered in filtering municipal water supplies, which can be as low as $0.01/1000 gal.

pH Adjustment

The pH of the feed to the column must be acidic. As indicated in Fig. 4, the actual pH affects color removal. Thus, costs of acidification must be balanced against column operating characteristics and costs.

Use of chlorination stage effluent for pH adjustment is desirable since color contained in this effluent is also removed. The disadvantages of using chlorination extract are twofold. First, operating costs will increase somewhat as more column feed and effluent must be handled. Second, sodium chloride is added to the white liquor system, assuming white liquor is used to regenerate the column, which may cause a chloride problem in the recovery system. For the effluents used in this study, approximately 2.5 volumes of chlorination effluent were required for each volume of caustic effluent to reduce the pH to 2.5.

pH control can also be achieved by using purchased concentrated acids. Sulfuric acid is probably the most economical. Assuming a caustic extract with pH 11, approximately 270 gallons of 100% H_2SO_4 would be necessary to adjust the pH of 1,000,000 gallons of bleach effluent to pH 2.

A simple comparison of costs is not the best method of judging which acidification procedure should be used. A study of the color of the various effluent streams should also be made. Table III gives data on two mills. For Mill A, color removal from the caustic extraction stage effluent would have to average 88% if proposed color standards (with a margin of safety) were to be met. Calculations show that if chlorination stage effluent is used for acidification, then only 80% color removal from the combined effluent is necessary to meet the desired standard of 100 pounds of color per ton of pulp.

TABLE III

COLOR REMOVAL ESTIMATES FOR TWO
BLEACHED KRAFT MILLS

	Mill A (1)	Mill B
Bleached pulp, ton/day	700	380
Wood makeup	80% HW	60% SW
AEB[a] volume, gal/ton of bleached pulp	2,420	3,000
AEB volume, gal/day	1,690,000	1,140,000
AEB color, lb/ton	152	219
Total mill color, lb/ton	234	274
1983 Regulations, average daily discharge, lb/ton	130	130
Discharge with safety margin, lb/ton	100	100
Color to be removed, lb/ton	134	174

[a]AEB = alkaline extraction stage bleach effluent.

For Mill B, 80% color removal from the caustic extract effluent alone would be sufficient to have the total mill effluent meet the desired level of 100 lb of color/ton of pulp. Calculations show that use of chlorination stage effluent for acidification requires only 67% of the total color to be removed.

Resin Requirements

The amount of resin required is a fairly straightforward calculation, once certain experimental parameters are known.

Let F = feed rate, gal/hr

C = color of feed, lb/gal

X = color capacity of the resin at a given operating condition and percent removal (obtained from experiments), lb/gal

R = regeneration time, in hours (obtained from experiments)

S = feed rate in bed volumes per hour

The procedure is to choose S and compute the volume of resin from the equation:

$$V = F/S$$

where V = volume of resin in gallons. The amount of time the resin bed can be operated at this rate is given by:

$$t = \frac{X \cdot V}{F \cdot C}$$

The total cycle time is given by

$$T = t + R$$

As long as the adsorption time, t, is greater than the regeneration time, R, only two beds would be required; one adsorbing color and the other either being regenerated or in a standby mode. If t is less than R, at least three beds would be required.

For most conditions, X will be chosen so that the effluent meets some desired criterion, such as 80% cumulative removal. The design procedure then reduces to tabulating costs at various values of S and choosing the minimum. Table IV gives estimates of operating times for the mill effluent studied in these experiments. The first part (A) of the table indicates resin requirements assuming the caustic extract is acidified with H_2SO_4 with virtually no increase in feed volume. The second part (B) of the table estimates resin requirements if chlorination effluent is used to acidify the caustic extract. The data in Table IV indicate the desirability of using chlorination stage effluent to acidify the caustic effluent.

TABLE IV

RESIN REQUIREMENTS FOR DECOLORIZATION

Mill Characteristics for Designing Adsorption System:

Caustic effluent

Flow	1,200,000 gpd
pH	10.5
Color	8,800 mg/liter
Temperature	50°C

Chlorination effluent

Flow required	3,000,000 gpd
pH	2.0
Color	650 mg/liter

Color removal

80% Removal	Maximum load 0.194# of color/gallon resin
67% Removal	Maximum load 0.751# of color/gallon resin

Adsorption System Design

A. 80% Removal
(Acidification with H_2SO_4)

F/V (bed volumes/hour)	0.5	1	2
Resin volume (gallons/bed)	100,000	50,000	25,000
Load time (hours)	5.29	2.64	1.32
Regeneration time (hours)	1.25	1.25	1.25
Cycles/day	3.67	6.17	9.34
Excess to white liquor systems (gpd)	184,000	155,000	117,000

B. 67% Removal
(Acidification with Chlorination Effluent)

F/V (bed volumes/hour)	6	10	12	16
Resin volume (gallons/bed)	29,166	17,500	14,583	10,937
Load time (hours)	5.34	3.18	2.65	1.99
Regeneration time (hours)	1.25	1.25	1.25	1.25
Cycles/day	3.64	5.42	6.15	7.41
Excess to white liquor system (gpd)	53,082	47,425	44,842	40,521

Regeneration

A caustic solution is necessary to regenerate the resin columns. Rock, et al. (1) in their pilot study concluded that either white liquor or weak wash could be used to regenerate the resin. In either case it was necessary to return more column eluate to the white liquor system than was used to regenerate the column. They indicated that the excess volume was necessary to ensure the complete return of sodium to the system. When white liquor was used, about 0.4 bed volume of excess liquid had to be returned to the white liquor system. No estimates were given for the excess volume required when weak wash was used as a regenerate. Thus, in either case a slight increase in evaporator capacity is necessary. Calculations by Rock, et al. (1) indicated that this increase was about 5%. To be balanced against this increase in evaporator cost was the loss in sodium if the excess were not returned to the white liquor system. For the calculation of the economics of the process, they assumed that the sodium recovery is complete.

Economics

The basis for our economic studies is the effluent characterizations given in Table IV. Cost data are taken from Rock, et al. (1) and updated to these specific design conditions. Equipment and material are updated using the Marshall and Stevens index to compensate for inflation. Analysis of Rock, et al.'s data indicate that a six tenths scale-up factor is feasible; that is, the following design equation is useable.

$$\text{Cost}_{\text{size 2}} = \text{Cost}_{\text{size 1}} \left(\frac{\text{Size 2}}{\text{Size 1}}\right)^{0.6}$$

The size measure used for the decolorization equipment is the cubic feet of resin employed.

The basis for the capital costs are given in Table V. The capital and operating costs are given in Table VI. As is evident from Table VI, decolorization of the combined chlorination and caustic effluent is economically desirable. By combining the effluents, a smaller total decolorization is needed in order to enable the mill to meet proposed standards. This, in turn, allows smaller adsorption columns to be used.

TABLE V

BASIS FOR ECONOMIC STUDIES

Caustic flow	1,200,000 gpd
Chlorine stage flow	3,000,000 gpd
Sulfuric acid for neutralization	270 gal/MM gal of caustic effluent

Resin Volume ft^3

80% Removal
(H_2SO_4 used for pH adjustment)

Load Rate	0.5 BV/hour	1 BV/hour	2 BV/hour
Resin	26,700 ft^3	13,400 ft^3	6700 ft^3

67% Removal
(Chlorination stage effluent used for pH adjustment)

Load Rate	10 BV/hour	12 BV/hour	16 BV/hour
Resin	4200 ft^3	3900 ft^3	2900 ft^3

Our calculations show that decolorizing the combined effluent with adsorption techniques is highly competitive with the "massive lime" process. The "massive lime" treatment costs about $0.50 for 1000 gallons of effluent, or about $1.50/ton if only the caustic stream is treated. This process must achieve at least 80% color removal if none of the other streams (e.g., the

chlorination stage effluent) is to be decolorized. If it doesn't, then some other stream must be treated and its costs added to those of the lime treatment.

TABLE VI

ECONOMIC ANALYSIS

	80% Removal (2 BV/hour)	67% Removal (16 BV/hour)
Capital cost ($MM)		
Equipment	1.56	0.94
Resin cost (at $92/ft^3)	0.62	0.27
Operating costs ($/ton)		
Resin replacement	0.49	0.22
H_2SO_4 usage ($50/ton, 100% basis)	0.31	
Electricity (2¢/kw-hour)	0.08	0.26
Repairs and maintenance (3% of equipment)	0.37	0.23
Depreciation (20 yr, straight line)	0.62	0.37
Evaporation cost ($4/M gal evaporated)	1.23	0.43
Total operating cost, $	3.10	1.51

One advantage the adsorption process has is that the treatment process can be easily expanded. With the addition of more columns, more waste can be handled, or greater removal can be obtained. Backup equipment is easily provided, although at a cost. Another advantage is that the concentrated solutions from the regeneration step are burned in the black liquor recovery furnace. The effect of these color bodies on the pulping process needs further investigation, however.

CONCLUSIONS FOR PART I

Based on limited experimental data, adsorption of color bodies from kraft mill effluents onto XAD-8 resin appears economical. The best operating mode is to use the chlorination stage effluent to adjust the pH of the caustic stage effluent to about 2.5, and then effect approximately 67% removal. Cost data indicate that this process compares favorably with massive lime treatment. The costs are preliminary, however, and are based on laboratory data and estimated resin life. A significant change in resin life would change the operating cost significantly.

PART II. COLOR REMOVAL BY ULTRAFILTRATION

INTRODUCTION

The concentration of colored material in kraft alkaline extraction bleach stage (AEB) effluents by reverse osmosis and ultrafiltration has been described extensively for cellulose acetate membranes (4,5) and, in a few cases, for noncellulosic membranes (6,7). Since the cellulose acetate membranes require lower pH and moderate temperature, much research has been carried out to develop ways for effecting ultrafiltration at higher pH and temperatures. The dynamic membranes have shown promise (8) but are considered less desirable than the plastic films (e.g., cellulose acetate, polysulfone) which are more apt to be free from irreversible plugging and, therefore, lend themselves to simple cleaning techniques. The Institute of Paper Chemistry staff requested the Westinghouse Electric Corporation (WEC) to develop a polysulfone membrane which would be usable at higher pH and temperatures for the ultrafiltration of mill effluents such as the highly colored kraft alkaline extraction effluents, kraft wash waters, spent sulfite liquors and kraft black liquors. WEC subsequently provided the Institute with two of their modules made of 9.25 sq ft sandlogs with the desired polysulfone membranes, which proved to be effective for concentrating colored material from kraft bleach effluents and kraft black liquors. However, when 5% spent sulfite liquor was concentrated in these modules, a general decline in flux rate (loss in porosity) was observed over a 2,200 hour testing period, despite periodic cleanup with a commercial enzyme detergent. Although some loss in porosity was regained when alkaline EDTA solutions were used for cleaning purposes, the regain was never 100%.

Ultrafiltration using cellulose acetate membranes is generally carried out at pressures below 200 psi because most applications have found little benefit in operating at higher pressures (9). The present study indicates possible benefits of high pressure operations using polysulfone membranes in concentrating alkaline extraction bleach effluents. Some preliminary studies on a kraft pulp wash water sample are also reported.

EXPERIMENTAL

The two modules used in the experiments described below were numbered 1022 and 489 by the manufacturer and had flux rates for Orange County, California, tap water of 45 gallons per square foot per day (gfd) at 25°C and 100 psi with 10% rejection (based on conductivity). The modules were fed in series by a Milroyal Duplex piston pump from a 55-gallon reservoir. A schematic diagram of the arrangement appears as Fig. 7. Steam was passed through the heat exchanger to obtain the elevated temperatures and tap water to maintain some of the lower temperatures.

The analytical data on the feeds used in this portion of the study have been already reported in Table I. The analysis was carried out according to the standard methods or the modifications described in IPC procedures.

EDTA washups were carried out by introducing 200 milliliters of Versene in 14 liters of H_2O and recirculating for different lengths of time through the modules with and without applied pressure.

RESULTS AND DISCUSSION

Alkaline Extraction Bleach Effluent

The performance of both modules was similar when alkaline extraction bleach effluent was processed. The results on Runs 1 and 2 are given in Table

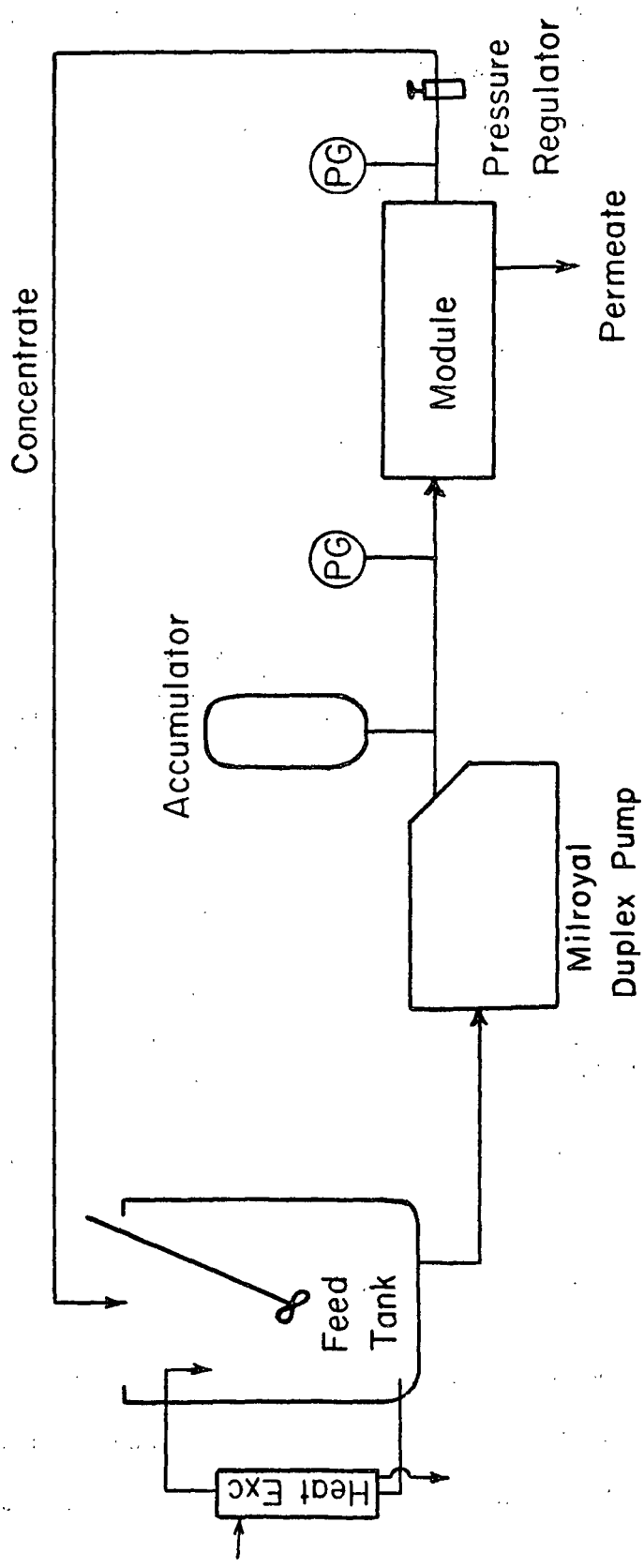

Figure 7. Schematic Diagram for Ultrafiltration Experiments

VII. The data for Run 1 show that rejections of 99.8% color and 85% solids were achieved at 50°C and 300 psi, while maintaining flux rates between 28 and 36 gfd. Run 2 was carried out at higher temperatures (69-75°C) and showed slightly lower rejections but almost double the flux rates.

TABLE VII

ULTRAFILTRATION CONCENTRATION OF ALKALINE EXTRACTION EFFLUENT SOLIDS

Run 1

Feed: 270 Liters of Effluent, Sample No. 121, pH 11.2, 48-51°C, 3.9 g/liter 8,260 Pt-Co Color Units.

Pump: Milroyal Duplex, 300/250 psi, 5 gpm.

	Color Rejection, %		Solids Rejection, %		Flux Rate, gfd	
Conversion, %	Module 1022	Module 489	Module 1022	Module 489	Module 1022	Module 489
0	99.6	99.5	63.1	73.3	30	28
86	99.8	99.9	82.4	86.8	35	38
97.2	99.3	99.7	84.3	88.4	32	36

Run 2

Feed: 180 Liters of Effluent, Sample No. 121, pH 11.2, 69-75°C. Other conditions the same as above.

0	98.2	98.7	54.1	65.2	78	104
72	99.6	99.8	72.0	76.7	69	80
94.4	98.7	99.4	80.4	83.5	52	69

While neither temperature is compatible with cellulose acetate membranes, the polysulfone membranes perform well at temperatures characteristic of typical alkaline extraction stages (70°C) and their washer seal box effluents (48°C).

Several recycle runs were carried out at different pressures to more nearly approximate flux rates which might be maintained for extended periods of time. The variation in pressure is important, since ultrafiltration is usually done at low pressure (<200 psi) (10).

Figures 8 and 9 show the increase in flux rate for the two modules while adjusting the pressure from 200 to 400 psi in 50-pound increments. Fifteen minutes were allowed for equilibrium to be established before taking flux readings. While the effect was reversible, there was a displacement to lower flux rates while decreasing the pressure back from 400 to 200 psi. This loss of flux could reflect a compaction of the membrane which was not reversed with the 15 minutes time allowed for equilibration. While the pressure effect is impressive for short periods of time, the effect of longer operations at different pressures is required to establish the usefulness of such observations. Several recirculating runs were then carried out for extended periods of time and the flux rates compared.

The results on high pressure ultrafiltration of recycled alkaline extraction effluent are given in Table VIII and plotted in Fig. 10. Run 10 at 300 psi showed, after 5 days, a flux rate decline to 12 gfd for both modules, while at 200 psi after 6 days (with a lower initial water flux) the flux rate was still at about 25 gfd. Graphs of the flux decline, Fig. 10, showed that the higher initial flux rates for 300 psi lasted for at least 50 hours. Operation at 400 psi, Run 12, likewise showed better initial flux rates but a greater drop after 70 hours of operation. To confirm the apparent beneficial effect of operating at elevated pressures, two additional runs were made with a new feed. Run 13 at 400 psi showed significantly greater flux rates over the three days of testing than the

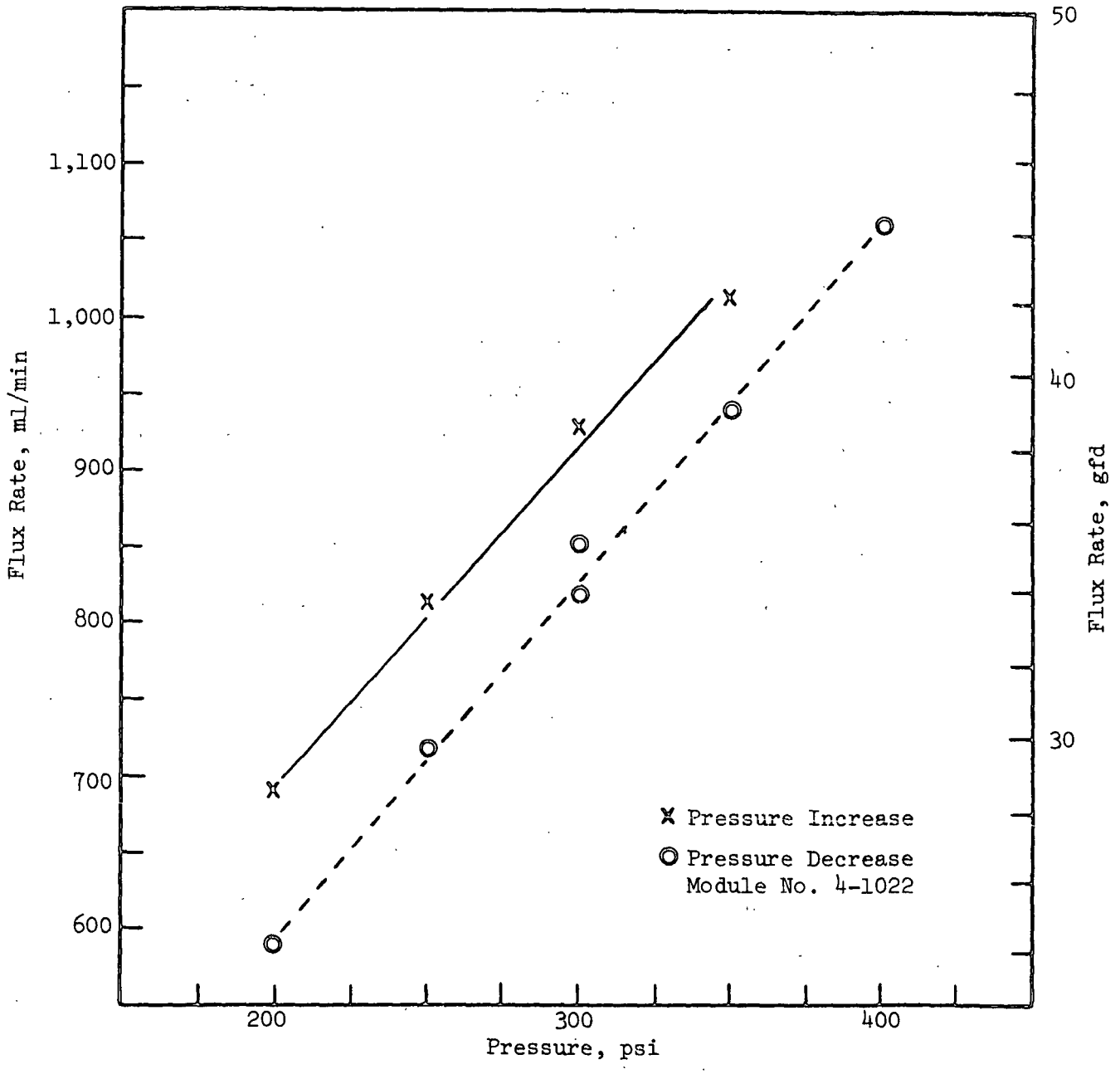

Figure 8. Effect of Pressure on Ultrafiltration Flux Rate (Module No. 4-1022)

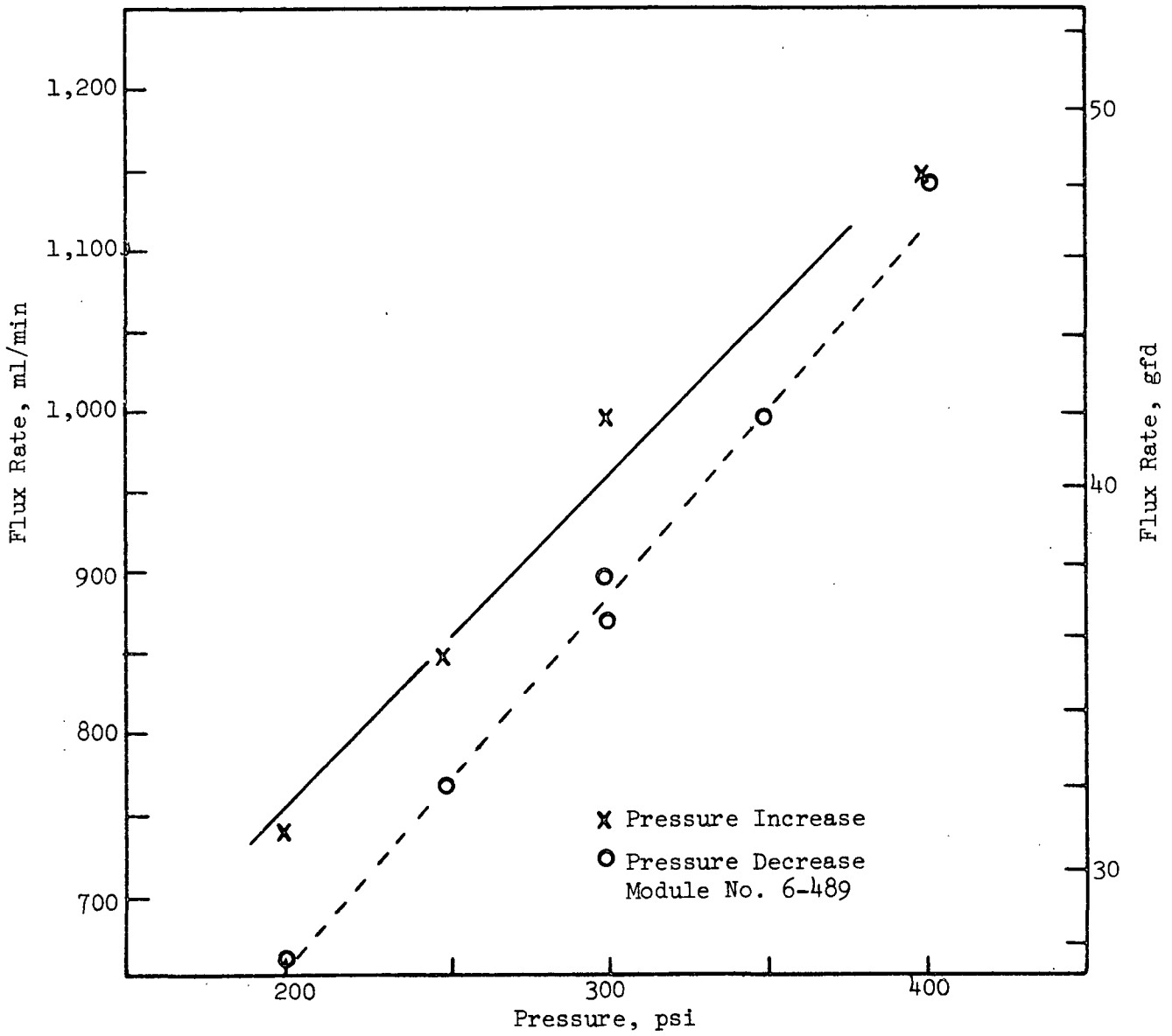

Figure 9. Effect of Pressure on Ultrafiltration Flux Rate (Module No. 6-489)

TABLE VIII

LONG TERM, HIGH PRESSURE RECYCLE OPERATION

	Time, days	Color Rejection, %		Solids Rejection, %		Flux Rate, gfd	
		Module 1022	Module 489	Module 1022	Module 489	Module 1022	Module 489
Run 10							
Feed No. 123							
Inlet pressure = 300 psig	0	97.4	96.3	53.1	56.0	52.8	35.3
Pressure drop = 60 psi	5	97.2	99.1	78.9	40.5	12.0	11.9
Run 11							
Feed No. 123							
Inlet pressure = 200 psig	0	97.4	97.3	48.0	53.0	37.1	42.0
Pressure drop = 75 psi	6	98.0	98.5	46.0	--	24.8	24.4
Run 12							
Feed No. 123							
Inlet pressure = 400 psig	0	99.3	99.0	65.5	57.4	54.6	54.6
Pressure drop = 70 psi	5	97.8	98.4	60.2	63.7	20.6	21.0
Run 13							
Feed No. 128							
Inlet pressure = 400 psig	0	98.6	97.7	54.8	60.4	50.4	51.4
Pressure drop = 70 psi	3	97.6	98.0	--	60.1	16.1	16.2
Run 14							
Feed No. 128							
Inlet pressure = 200 psig	0	97.1	98.3	46.0	52.0	36.2	35.1
Pressure drop = 75 psi	3	97.2	96.6	55.5	57.7	12.4	11.0

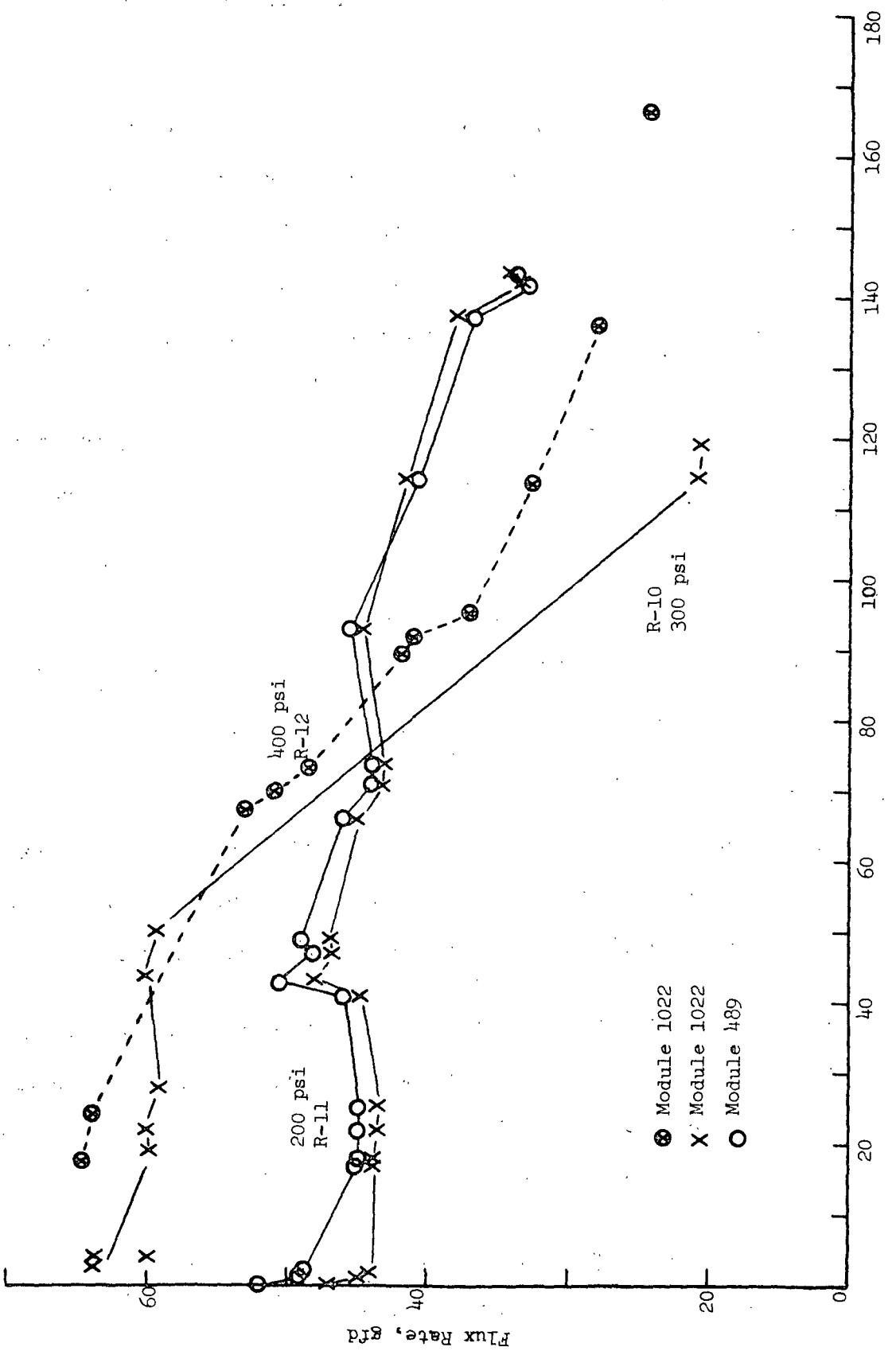

Figure 10. Flux Decline During High Pressure Operation

200 psi run despite the greater water flux for the modules prior to the run at 200 psi. Figure 11 shows the flux rates for the two runs.

The above data imply that with regular cleaning at intervals before the flux rates begin to decline the membranes would be more efficient at the higher operating pressures. To show the effect of regular 15-minute cleanups with Versene, a similar recycling run was carried out with a shutdown every 24 hours for a washup with and without applied pressure. Figure 12 shows the flux rate over a 100-hour operating period with four cleanups. While the lowest flux rates are not declining, it is obvious that the highest flux rates are not being recovered. A more drastic washing procedure is apparently required to keep the modules performing at maximum efficiency.

Checks on rejection of color and solids during the tests on kraft alkaline extraction bleach effluent showed consistently 98.2 to 98.7% color and 55-63% solids rejections for the two modules.

Kraft Pulp Wash Water

A sample of a kraft pulp wash water with a solids content of 3.1 grams per liter and 864 mg/liter color value was also subjected to ultrafiltration on the polysulfone membranes. Table IX shows the results of a recycling run.

Repeated runs showed consistently lower solids rejection, suggesting that the 92.3% solids rejection for Module 1022 was an erroneous result. The run was for two days and showed each module leveling off at about 18 gfd with color rejections of 97.3 and 96.6% for the two modules.

A concentrating run from 3.4 g/l to 11.2 g/l also showed a leveling off of flux rate around 18 gfd. Table X summarizes these data.

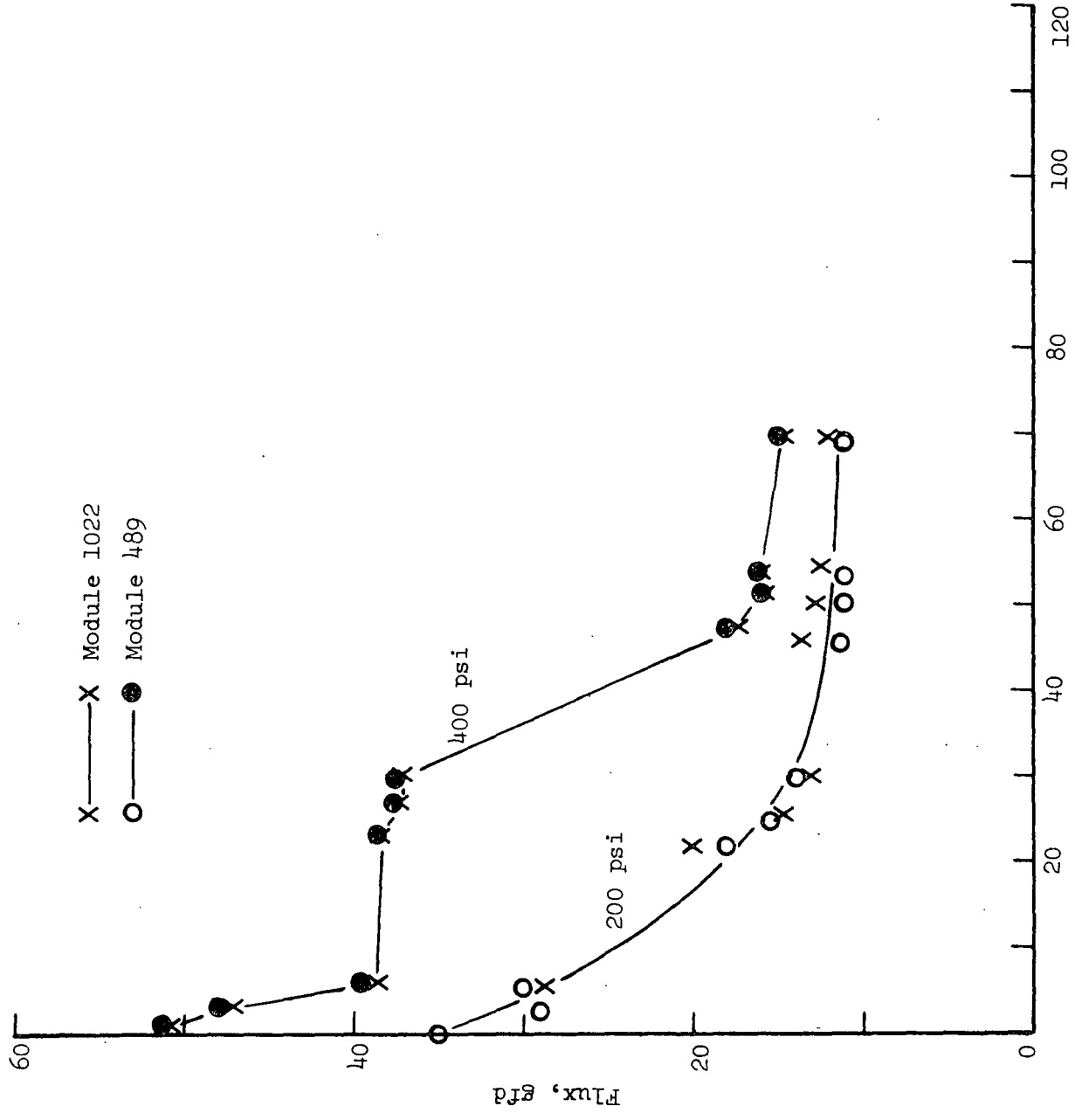

Figure 11. Flux Rate Decline with Time

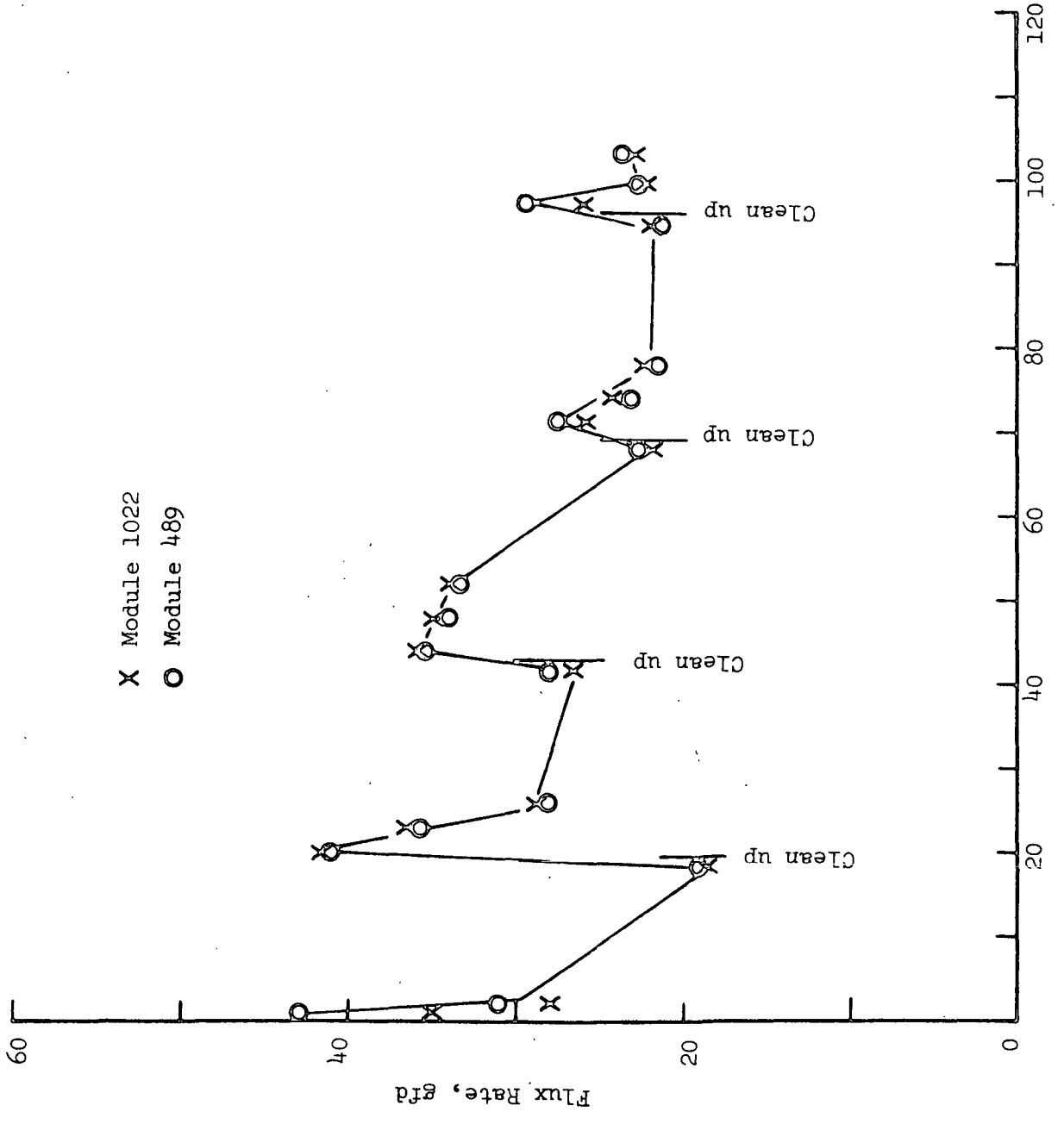

Figure 12. Effect of Membrane Cleaning on Flux Rates

TABLE IX

RECYCLE ULTRAFILTRATION OF
KRAFT PULP WASH WATER

Feed: 180 Liters of wash water, Sample No. 125, 40°C, 3.1 g/l solids, 864 Pt-Co color units

Inlet Pressure: 400 psig; pressure drop 140 psi; flow rate 4.5 gpm

Time, hours	Color Rejection, %		Solids Rejection, %		Flux Rate, gfd	
	Module 1022	Module 489	Module 1022	Module 489	Module 1022	Module 489
0	96.1	89.7	92.3	64.6	20.0	19.7
24	96.9	95.8	68.6	71.9	18.0	18.7

TABLE X

ULTRAFILTRATION CONCENTRATION OF
KRAFT PULP WASH WATER SOLIDS

Feed: 180 Liters of wash water, Sample No. 125, 37-41°C, 3.4 g/liter solids, 1,008 color units at start of sampling

Pump: Milroyal Duplex, 400/260 psi, 4.5 gpm

Solids Level, g/liter	Color Rejection, %		Solids Rejection, %		Flux Rate, gfd	
	Module 1022	Module 489	Module 1022	Module 489	Module 1022	Module 489
3.4	96.9	95.8	68.6	71.9	26.7	73.8
7.1	95.8	88.2	73.4	64.3	19.4	23.9
9.3	95.5	--	70.4	--	18.9	18.5
11.2	99.1	98.0	78.3	48.9	18.7	18.2

The color units increased from 1,008 to 4,440 during the run. The results showed that the polysulfone membrane has good rejection properties for color bodies in the kraft pulp wash water which was studied. Whether or not higher flux rates could be maintained in a new module with an appropriate cleaning schedule remains to be determined.

Several aspects of the ultrafiltration work on bleach effluents and pulp wash waters suggest that the rejection and flux rate data should not be considered highly reproducible. The modules had a complicated history, the feed liquor changes with age and some barrels stood for 3 or 4 weeks before being used. During recycling runs the feed was also subjected to repeated pressurization and pressure release which usually resulted in considerable aeration. These factors perhaps caused some changes such as precipitation of residues which would not otherwise have separated out of solution.

Nevertheless, several aspects of the work are of importance. The color rejection by the membrane was outstanding (98% plus) at temperatures above 70°C. Pressures above 200 psi showed overall increased flux rates, suggesting that elevated pressures would be more efficient for such ultrafiltration. To get the benefit of the higher flux rates in the early phases of operation, an effective cleaning regime would have to be developed.

The polysulfone membrane appears very durable. It has been exposed to pH values in excess of 11 for over 500 hours, many of which were over 70°C. The membranes have also been allowed to dry out. Although their flux rates at the lower temperatures are lower than those for comparable cellulose acetate membranes, with adequate cleaning techniques, the membrane might still be as efficient as a cellulose acetate membrane.

As a color concentrating technique, ultrafiltration provides a possible alternative to other methods, but the technology needs considerable work before the economics of the method can be adequately assessed. Additionally, disposal methods for the concentrated solutions must be developed.

CONCLUSIONS FOR PART II

Ultrafiltration with polysulfone membranes shows improved flux rates as the pressure is increased from 200 to 400 psig. These membranes show excellent color rejection over a wide range of temperature and pH. Development of cleaning procedures are necessary to maintain the high initial flux rates. The cleaning schedule must be developed and studies made to determine the membrane life. Membrane cost will probably be an important economic factor, thus requiring the polysulfone membranes to be produced commercially before an economic analysis can be made.

ACKNOWLEDGMENTS

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Arthur A. Webb
Research Fellow
Effluent Processes Group

Peter E. Parker
Research Fellow

Hardev S. Dugal
Director
Division of Industrial &
Environmental Systems